

Stereoselectivity of Octahedral Complexes. V¹ Solvent Influence on the Relative Diastereomer Abundances of Tris[(+)-3-Acetylcamphorato]vanadium(III)

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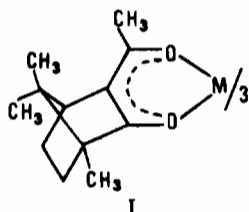
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Analysis of the isotropically shifted pmr signals of the labile complex, tris[(+)-3-acetylcamphorato]vanadium(III), reveals the number of diastereomers present and their relative abundances. A rather marked solvent effect on the diastereomer proportions has been found. The ratio of concentrations of Δ -trans and Λ -trans diastereomers varies from a minimum of 0.31 in chloroform solution to a maximum of 0.97 in benzene over seven solvents investigated. Attempts to interpret the variation of isomer abundances in terms of solvent properties such as polarity, coordination tendency, or hydrogen bonding ability have not been successful. The results indicate, however, that for labile complexes solvent-solute interactions may have a significant influence on stereoselectivity, a phenomenon generally attributed to intramolecular steric interactions alone.

Introduction

Investigations in this laboratory over the past several years have been concerned with stereoselective phenomena in tris complexes of chiral, bidentate ligands in which the chelate ring moiety is planar and conjugated.¹⁻⁶ Several diastereomers are expected for complexes of this general type, and the term stereoselectivity used here refers to deviations from the statistically expected proportions of diastereomers.

Although several ligand systems differing in steric requirements of groups attached to the asymmetric centers have been investigated, the largest body of results at present has been obtained from complexes of general structure I, where the ligand is (+)-3-acetylcamphorate and M represents a trivalent transition metal ion. These complexes are neutral and soluble in a variety of organic solvents.



(1) Part. IV: R.M. King and G.W. Everett, Jr., *Inorg. Chem.*, **10**, 1237 (1971).

The four possible diastereomers, Δ -trans, Λ -trans, Δ -cis and Λ -cis,⁷ can be separated chromatographically for the relative inert complexes of Co^{III},^{1,8} Cr^{III},¹ and Ru^{III}.⁶ For the Co^{III} and Cr^{III} complexes, diastereomer abundances follow the order Λ -trans > Δ -trans > Λ -cis > Δ -cis with Δ -trans/ Λ -trans ratios of 0.61 and 0.79, respectively.¹ The statistically expected Δ -trans/ Λ -trans ratio is 1.0, and the overall statistical trans/cis isomer ratio is 3.0. The two trans diastereomers for the Ru^{III} complex have nearly identical abundances. In the case of the Co^{III} complex stereoselectivity is probably thermodynamically controlled. However kinetic factors are believed to be largely responsible for the relative isomer abundances in the Cr^{III} and Ru^{III} complexes.

Tris[(+)-3-acetylcamphorato]vanadium(III), I (M = V), hereafter abbreviated V(atc)₃, was one of the first complexes in this series to be studied.² The diastereomers cannot be separated owing to the lability of the complex; however isomerization is slow on the nmr timescale, and proton nmr (pmr) may be used to investigate stereoisomerism. Although V(atc)₃ is paramagnetic, the extremely short electron spin relaxation time permits observation of reasonably narrow resonance signals of ligand nuclei. These resonance signals experience isotropic shifts⁹ which have the effect of spreading the spectrum and vastly increasing resolution. Resonance signals arising from individual diastereomers of V(atc)₃ in chloroform solution were assigned previously, and a Δ -trans/ Λ -trans diastereomer abundance ratio of 0.31 was determined by signal integration.² It was assumed that since the complex is labile this ratio represents an equilibrium distribution of the two diastereomers which is determined by their relative intramolecular steric interactions. The nature

(2) Y.T. Chen and G.W. Everett, Jr., *J. Amer. Chem. Soc.*, **90**, 6660 (1968).

(3) G.W. Everett, Jr. and Y.T. Chen, *ibid.*, **92**, 508 (1970).

(4) K.S. Finney and G.W. Everett, Jr., *Inorg. Chem.*, **9**, 2540 (1970).

(5) J.E. Gray and G.W. Everett, Jr., *ibid.*, **10**, 2087 (1971).

(6) G.W. Everett, Jr. and R.M. King, *ibid.*, **11**, 2041 (1972).

(7) The symbols Δ and Λ represent right- and left-hand helicity, respectively, about the C₂ or pseudo-C₂ axis of the complex in accord with the recommendations of IUPAC. *Inorg. Chem.*, **9**, 1 (1970). Cis and trans refer to facial and meridional arrangements, respectively, of identical groups about the octahedral coordination sphere.

(8) C.S. Springer, Jr., R.E. Sievers, and B. Felbush, *Inorg. Chem.*, **10**, 1242 (1971).

(9) (a) D.R. Eaton and W.D. Phillips, *Advan. Magnetic Resonance*, **1**, 103 (1965); (b) E. deBoer and H. van Willigen, *Prog. Nucl. Magn. Resonance Spectrosc.*, **2**, 111 (1967); (c) R.H. Holm, *Acc. Chem. Res.*, **2**, 307 (1969).

of these steric interactions, however, is not readily apparent from examination of space-filling molecular models.

Since publication of the original work on $V(atc)_3$ we have had occasion to examine pmr spectra of the complex in solvents other than chloroform. A rather marked solvent dependence of diastereomer proportions is found among a series of organic solvents. Results of a study of this solvent dependence are presented in this paper.

Results

It has been pointed out in several previous papers^{2,3,6} that for *trans* isomers of complexes I three pmr signals may arise from each kind of ligand proton. A single resonance is expected for each kind of proton in a *cis* isomer. Thus in a mixture of all four diastereomers, up to eight pmr signals per proton type may be observed.

Proton nmr spectra of $V(atc)_3$ in seven solvents were recorded. In each case two groups of signals appear at low field (15-55 ppm downfield of tetramethylsilane) which are well separated from other resonances and from each other. These are shown in Figures 1 and 2. The group at lowest field, consisting of 6-8 signals depending upon the solvent, is assigned to the 3-acetyl-methyl on the basis of its disappearance when the complex is deuterium labeled at this position.^{2,10} The other group of signals at low field has an overall area equal to 1/3 that of the acetyl methyl group and has been assigned to one of the camphor methylene protons.² Signals arising from other ligand protons are not sufficiently well resolved for stereochemical analysis.

It may be seen from inspection of Figures 1 and 2 that the overall pattern of signals is quite dependent upon the solvent. On the other hand, closer examination reveals a straightforward correlation among the individual methyl signals from one solvent to another. This is discussed in detail below. First, several relationships (not necessarily independent) involving pmr signal areas, which will aid in assigning individual resonances, are outlined. If the areas of all signals in the methyl and methylene groups could accurately be determined, the following relationships would permit facile interpretation of the spectra: (1) Assuming no resonances are accidentally coincident, a *trans* isomer will produce three signals of identical area within each group. (2) Again assuming no coincidences, within a group any signal having unique area must arise from a *cis* isomer. (3) A signal assigned to a specific diastereomer in the methylene group must have 1/3 the area of a signal in the methyl group assigned to the same diastereomer. (4) The abundance ratio of any two isomers determined from areas of signals in one group must match that obtained from areas in the other group. In practice, two or more signals in each group are coincident or severely overlapping, so ma-

ximum advantage of (1)-(4) cannot be taken as a result of uncertainty in the signal areas.

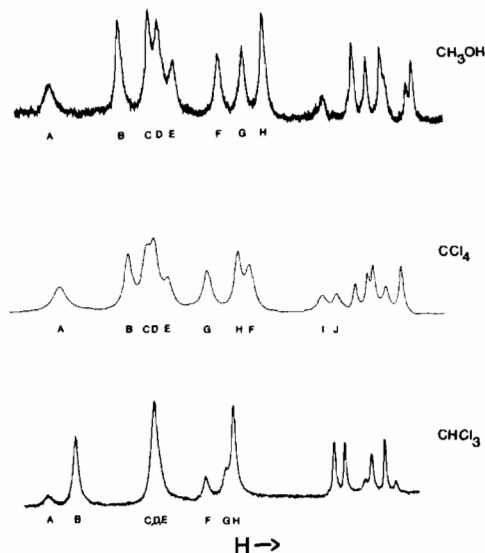


Figure 1. 100 MHz proton nmr spectra of $V(atc)_3$ at 32°. Only the low-field methyl and methylene signals are shown. Spectra shown are not recorded at the same scan rate.

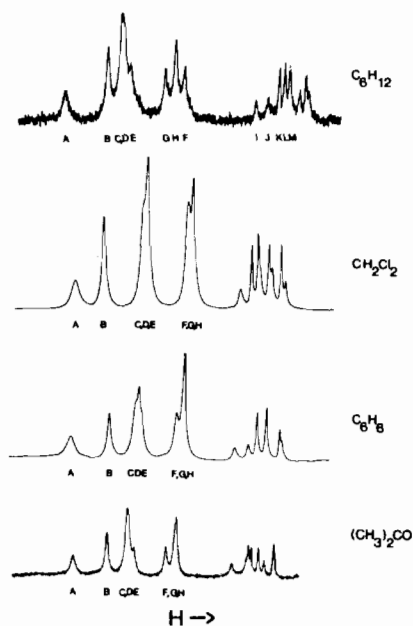


Figure 2. 100 MHz proton nmr spectra of $V(atc)_3$ at 32°. Only the low-field methyl and methylene signals are shown. Spectra shown are not recorded at the same scan rate.

Using relationships (1)-(4), partial assignments of the methyl and methylene resonances shown in Figures 1 and 2 can be made. In all cases the relative proportions of the two *trans* diastereomers can be determined. Areas of signals arising from the *cis* isomers could not be determined accurately in all cases. Signal assignments for spectra in methanol, carbon tetrachloride, and chloroform solution, shown in Figure 1, will be discussed in detail. Simple ex-

(10) Deuteron nmr spectra of the deuterium labeled complex reveal a group of signals nearly identical in appearance with the group at lowest field in the pmr spectrum, cf. G.W. Everett, Jr. and Ann Johnson, *J. Amer. Chem. Soc.*, **94**, 6397 (1972).

Table I. Solvent Dependence of Relative Diastereomer Abundances for Tris [(+)-3-acetylcamphorato]vanadium(III).

Solvent	ϵ^b	Ratio of Δ - <i>trans</i> / Λ - <i>trans</i> Concentrations ^a	
		methyl signals	methylene signals
CHCl ₃	4.8	0.31 ± 0.02 ^c	0.34 ± 0.05 ^c
CH ₂ Cl ₂	8.64 ^d	0.58 ± 0.04	0.52 ± 0.05
(CH ₃) ₂ CO	20.2	0.60 ± 0.06	0.61 ± 0.03
C ₆ H ₁₂	2.03	0.61 ± 0.06	0.58 ± 0.02
CH ₃ OH	31.5	0.72 ± 0.04	—
CCl ₄	2.23	0.78 ± 0.07	0.72 ± 0.01
C ₆ H ₆	2.26	0.97 ± 0.03	—

^a Determined by integration of pmr signals recorded at 32°. See text for assumptions made in assigning configurations. Error limits shown are standard deviations from the mean of values determined by integration of several spectral. ^b Extrapolated to 32° using data from International Critical Tables, Vol. VI, McGraw-Hill, New York, N. Y., 1929, pp. 82-97, except where otherwise indicated. ^c Values from reference 2. ^d Extrapolated to 32° using value from Handbook of Chemistry and Physics, 40th Edition, Chemical Rubber Publishing Company, Cleveland, Ohio, 1958, p. 2513.

tension of the arguments used in interpreting these spectra allow assignments of the signals shown in Figure 2.

V(atc)₃ in Methanol. All eight acetyl methyl signals are present (A-H in Figure 1), demonstrating the existence of all four diastereomers. A pattern of four strong and four weak signals is evident. Within each set of four signals, three must arise from a *trans* diastereomer; the remaining one must represent a *cis* diastereomer. Signals A, F, and G have identical areas within experimental error, and these are assigned to the less abundant *trans* diastereomer. Signal E is of similar height to F and G, but this is probably the result of a contribution from the C-D envelope. The area of E is somewhat smaller than that of A, F, or G, thus it is tentatively assigned to the less abundant *cis* diastereomer. Support for the assignments of signals A, F, and G lies in the fact that signals corresponding to these for *V(atc)₃* in other solvents have equal areas in each case where measurement is possible (*vide infra*). Of the four more intense resonances, B and H have identical areas, and at least one of these must arise from the more abundant *trans* diastereomer. One of these signals could result from a *cis* isomer if the *cis:trans* ratio had the statistically expected value of 1:3. Relative areas of signals C and D are not accurately known, but at least one of these must be assigned to the more abundant *trans* diastereomer. Signals corresponding to B and H for *V(atc)₃* in other solvents (*vide infra*) have identical areas in all cases where accurate measurements can be made. Thus either the *cis:trans* ratio is statistical in each case or both B and H arise from a *trans* isomer. In either case the area of one of these signals is a measure of the concentration of the more abundant *trans* diastereomer in solution. The relative abundance of the two *trans* diastereomers is taken as the ratio of area of one of the signals A, F, or G to the area of B or H. The group of methylene resonances in this solvent is not as well resolved as the methyl group, and no attempt is made to assign signals in the methylene group.

Although *cis* and *trans* species are easily identified by nmr for complexes I, diastereomers differing only in helicity (eg. Δ -*trans* and Λ -*trans*) cannot be distinguished unambiguously by nmr alone. In order to facilitate discussion throughout this paper, the as-

sumption will be made that the order of diastereomer abundances for *V(atc)₃* is the same as that found in the *Co^{III}* and *Cr^{III}* complexes of the same ligand. Arguments have been presented previously in support of this assumption.² Absolute configurations for all diastereomers of the latter two complexes have been firmly established by a combination of methods.^{1,8,11} In accord with the above assumption we assign the Δ -*trans* configuration to the more abundant *trans* diastereomer and the Λ -*cis* configuration to the more abundant *cis* diastereomer.

V(atc)₃ in Carbon Tetrachloride. Again all eight methyl signals are resolved. The pattern closely resembles that found in methanol except that one of the signals labeled F or G in methanol is now upfield of signal H.¹² Within experimental error signals A, F and G have the same area, as do signals B and H. Reasonable assumption is that signal assignments made for *V(atc)₃* in methanol solution apply also to the spectrum in carbon tetrachloride. Accordingly, the Δ -*trans*/ Λ -*trans* abundance ratio is given by areas of A (or G)/B or by A (or G)/(H + F - G). In practice, results from these two methods were averaged over several spectra to give the value shown in Table I. Seven of the eight possible methylene signals are resolved in carbon tetrachloride solution, and the Δ -*trans*/ Λ -*trans* ratio may also be obtained from this group. It appears that signals I and J arise from the Δ -*trans* isomer because they have equal area and this area is 1/3 that of A or G. The signal at highest field is assumed to contain two resonances due to its relatively large area. Relationships (1)-(3) were applied, and (4) was upheld within error.

V(atc)₃ in Chloroform. Only six of the eight possible methyl resonances are apparent. This spectrum was discussed in detail previously,² and earlier assignments are consistent with those in the present paper. The pattern of methyl resonances may be related to the patterns found in methanol and carbon tetrachloride if the assumption is made that signals labeled C, D, and E in these solvents happen to be coincident in

(11) W. DeW. Horrocks, Jr., D.L. Johnston, and D. MacInnes, *ibid.*, 92, 7620 (1970).

(12) Since signals F and G have the same area, the labels are unimportant. The signal labeled F in the spectrum of *V(atc)₃* in carbon tetrachloride solution may or may not correspond to that labeled F in the spectrum in methanol solution. However it does correspond to signal F in the chloroform spectrum (see text).

Table II. Chemical Shift Values ^a for Tris[(+)-3-acetylcamphorato]vanadium(III) in Various Solvents.

	CHCl ₃	CCl ₄	CH ₂ Cl ₂	Solvent C ₆ H ₆	C ₆ H ₁₂	(CH ₃) ₂ CO	CH ₃ OH	
Methyl Group	50.9(A)	51.3(A)	51.5(A)	51.6(A)	49.5(A)	49.8(A)	52.4(A)	
	48.4(B)	44.7(B)	47.0(B)	45.5(B)	44.1(B)	44.5(B)	45.5(B)	
	41.1(C,D,E)	43.0(C)	40.1(C,D,E)	41.5 } (C)	42.3(C,D)	41.4(C,D)	42.7(C)	
	36.3(F)	42.5(D)	33.8(F,G)	41.0 } (D)	41.1(E)	40.4(E)	41.8(D)	
	34.5(G)	40.9(E)	33.0(H)	40.5 } (E)	36.6(G)	35.4(F)	40.7(E)	
	33.8(H)	37.0(G)		35.0 } (F)	35.3(H)	33.7(G,H)	36.5(F)	
		34.2(H)		33.9 } (G,H)	34.2(F)		34.4(G)	
		33.1(F)					32.5(H)	
	Methylene Group	24.6	25.9(I)	25.2	25.5	24.9(I)	24.7	27.4
		23.6	24.6(J)	23.4	23.3	23.3(J)	24.4	24.8
21.7		22.6	22.5	22.0	21.9(K)	22.1	23.5	
21.1		21.4	20.8	20.5	21.2(L)	21.5	22.2	
19.8		20.9	20.2	18.4	20.6(M)	20.5	19.9	
18.8		19.6	18.8	18.0	19.3	19.4	19.4	
		18.2	18.1		18.5	18.0		
					18.1			

^a In parts per million downfield of internal tetramethylsilane at 32°. Estimated errors are ±0.3 ppm. Letters in parentheses correspond to labels in Figures 1 and 2.

chloroform. This was verified by examining spectra of V(atc)₃ in CHCl₃-CCl₄ solvent mixtures. As the mole fraction of CCl₄ is increased, the envelope C, D, E gradually splits into three signals and B moves upfield away from A. Also, signals F and G shift in opposite directions relative to H with the result that the signal labeled F in the chloroform spectrum appears upfield of signal H in carbon tetrachloride. Signals A, F, and G have the same area and are assigned to the Δ -*trans* isomer. Similarly, signals B and H are of equal area and are attributed to the Λ -*trans* diastereomer. The average Δ -*trans*/ Λ -*trans* ratio is given in Table I. The increase in this ratio upon going from chloroform to carbon tetrachloride is readily apparent upon comparing the relative strengths of signals G, F, and H in the two spectra.

V(atc)₃ in Cyclohexane and Dichloromethane. In both these solvents all eight methylene resonances may be seen (Figure 2). In each case the pattern of four strong and four weak signals indicates a predominance of one *cis* and one *trans* diastereomer over the other two. Using relationships (1) and (2) outlined above, partial assignments of the methylene signals may be made, and the ratio of *trans* isomer abundances may be determined from this group. For example, in cyclohexane solution signals I and J are assigned to the Δ -*trans* diastereomer, whereas K, L, and M are believed to represent the Λ -*trans* isomer. The ratio of *trans* isomer abundances also may be determined from the group of methyl resonances in these two solvents, assuming the same signal assignments made for spectra in methanol, carbon tetrachloride and chloroform. Areas of signals A and B and the F-G-H envelope were used in this regard. The Δ -*trans*/ Λ -*trans* ratio found using the methyl group is compared to that obtained from the methylene group in Table I. Relationship (4) is obeyed within the limits of experimental error. Also relationship (3) was maintained.

V(atc)₃ in Benzene and Acetone. In these solvents neither the methyl nor the methylene group is fully resolved into the eight possible resonances (see Figure

2). However the pattern of methyl resonances in each case is very similar to that observed for V(atc)₃ in the other solvents discussed above, and the same signal assignments are assumed to be valid for benzene and acetone solutions. The ratio of *trans* diastereomers may be determined using areas of signals A, B, and the F-G-H envelope. In acetone solution the methylene group is fairly well resolved, and an attempt to obtain the Δ -*trans*/ Λ -*trans* ratio from that group was made. Values for the ratio of *trans* isomer abundances are compared in Table I.

Discussion

Chemical shifts of the acetyl methyl and methylene resonances of V(atc)₃ are solvent dependent as may be seen from Table II. Solvents are known to influence chemical shifts of solute nuclei in a number of ways,¹³ and no attempt is made here to explain these effects. Linck and Sievers have analyzed the effects of various solvents on chemical shifts of Al^{III} β -diketonates.¹⁴

Of primary interest to us is the influence of solvent on the diastereomer populations of V(atc)₃. The relative concentrations of the two *trans* diastereomers as a function of solvent are presented in Table I. Relative abundances of the two *cis* diastereomers could not be determined for all solvents and are not given. *Trans* isomer ratios obtained using the group of methylene resonances are in reasonable agreement with those determined from the acetyl methyl signals. In view of the lability of V^{III} complexes in general,¹⁵ it is reasonable to assume that a thermodynamically controlled distribution of isomers is present in each solvent. Thus the ratios given in Table I represent relative thermodynamic stabilities of the Δ -*trans* and Λ -*trans* diastereomers of V(atc)₃, species which differ

(13) Cf. L.M. Jackman and S. Sternhell, Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry, Second Edition, Pergamon Press, Oxford, 1969, pp. 104-113.

(14) R.G. Linck and R.E. Sievers, *Inorg. Chem.*, 5, 806 (1966).

(15) F. Basolo and R.G. Pearson, Mechanisms of Inorganic Reactions, Second Edition, John Wiley and Sons, Inc., New York, 1967, Chapter 3.

only in helicity about the pseudo-C₃ axis of the molecule. The statistical ratio of 1.0 is approached only in benzene solution. Deviations from this ratio in other solvents reflect the extent of stereoselectivity between the two diastereomers. This is most pronounced in chloroform solution where one isomer is present at roughly three times the concentration of the other.

Previously it has been assumed that stereoselective effects in tris-bidentate complexes are governed primarily by intramolecular (interligand) steric interactions or hydrogen bonds which differ among molecular diastereomers.^{2-4,16} This being the case, it is reasonable to assume that for complexes of a given chiral ligand the *relative* stabilities of diastereomers will not change upon changing the metal ion. Thus the Δ -*trans* configuration was assigned² to the more abundant diastereomer of V(atc)₃ in chloroform solution because the most abundant diastereomer of Co(atc)₃ was believed (and later proven¹) to have this configuration. This assignment is used in the present paper for convenience, however the configurational assignments for V(atc)₃ are rendered less convincing by the marked solvent influence on stereoselectivity.

In an effort to explain the observed solvent effects on diastereomer abundances for V(atc)₃, several factors have been taken into consideration. During thin-layer chromatographic separation of the diastereomers of Co(atc)₃,¹ Cr(atc)₃,¹ and Ru(atc)₃,⁶ the Δ -*trans* isomer has a larger R_f value than the Λ -*trans* isomer in each case, indicating that the Λ -*trans* isomer is the more polar of the two. Assuming that the ratios given in Table I represent Δ -*trans*/ Λ -*trans*, one might expect the ratios to decrease with increasing solvent polarity. However there is no obvious correlation of the ratios with dielectric constants, ϵ , of the solvents at 32° (the nmr probe temperature). In this regard it is of interest to note that in recent investigations of *cis-trans* isomerism in the tris(*N-p*-tolylpyridinaldimine) cobalt(II) cation¹⁷ and in tris(benzoylacetato)cobalt(III),¹⁸ no smooth variation in the *cis/trans* ratio with solvent ϵ was found.

Pmr measurements for V(atc)₃ were initially made on solutions approaching saturation in order to ensure adequate signal strength. The solubility of V(atc)₃ varies considerably from solvent to solvent, possibly causing differences in solute-solute interactions which could be interpreted as a solvent effect. In order to test for this behavior, spectra in CHCl₃, CH₂Cl₂, and CCl₄ were recorded at concentrations ranging from 10-50% of those of the original solutions. No change in the relative nmr signal areas could be detected in any instance.

It has been shown that CHCl₃ and CH₃OH form hydrogen bonds to tris- β -diketonate complexes of a number of metal ions.¹⁹ Presumably CH₂Cl₂ also has

this property. Although the lowest isomer abundance ratios in Table I are found for CHCl₃ and CH₂Cl₂, the change in ratio on going from CHCl₃ to CH₂Cl₂ is appreciable. In fact, the ratio found in CH₂Cl₂ solution is very close to the ratio found in C₆H₁₂ where hydrogen bonding is expected to be negligible. The ratio determined in CH₃OH solution is near the middle of the range of values. Thus it appears that hydrogen bonding by the solvent is not the predominant interaction influencing the isomer distribution. Neither does there seem to be any relationship between the coordinating ability of the solvent, e.g. CH₃OH and (CH₃)₂CO, and the extent of stereoselectivity.

In summary, no simple correlation of the isomer abundance ratios with solvent properties such as dielectric constant, coordinating tendency, or hydrogen bonding ability or with solute concentration is evident. A combination of various solvent-solute interactions is undoubtedly responsible for the isomer distribution in a given solvent. These interactions must differ only slightly between Δ -*trans* and Λ -*trans* diastereomers, since free energy differences are less than 1 kcal/mole in each case. Although the observed solvent effects cannot be interpreted at this time, it is clear that solvent interactions may have a pronounced effect on the relative thermodynamic stabilities of diastereomeric species. This may result in a variation of stereoselectivity with solvent for labile complexes. Thus attempts to rationalize stereoselective phenomena in these systems by consideration of intramolecular steric interactions alone is hazardous, and as pointed out previously by Gillard,²⁰ one must be "aware of preferred solvation as a source of stereoselectivity".

Experimental Section

(+)-3-Acetylcamphor and tris[(+)-3-acetylcamphorato]vanadium(III) were prepared and purified as previously described.² Chloroform-d₁, methylene chloride-d₂, methanol-d₄, acetone-d₆, benzene-d₆, and cyclohexane-d₁₂ were purchased from Stohler Isotope Chemicals, Inc., and were used as received.

Pmr spectra were obtained using a Varian Model HA100 spectrometer operating in the HR mode at 32°. Chemical shifts (Table II) were measured by standard side-banding techniques. Solutions for pmr experiments were prepared under a nitrogen atmosphere and sealed *in vacuo* in standard 5 mm nmr tubes. Tetramethylsilane (ca. 1% by volume) was included as an internal reference standard. Deuterated solvents were used where necessary to avoid baseline problems resulting from the strong solvent resonance at high spectrometer gain. Areas of individual resonances were measured with a polar planimeter. In some cases a DuPont Model 310 curve resolver was used in analyzing overlapping signals; otherwise the signals were resolved by hand.

The Δ -*trans*/ Λ -*trans* ratios shown in Table I were obtained in the following manner. Several spectra were recorded for a given solvent at different spectrometer scan rates and rf power levels. For each spec-

(16) (a) E.J. Corey and J.C. Bailar, Jr., *J. Amer. Chem. Soc.*, **81**, 2620 (1959); (b) J.H. Dunlop, R.D. Gillard, and R. Ugo, *J. Chem. Soc. (A)*, 1540 (1966); (c) J.H. Dunlop and R.D. Gillard, *Advan. Inorg. Chem. Radiochem.*, **9**, 185 (1966); (d) C.J. Hawkins, Absolute Configuration of Metal Complexes, Wiley-Interscience, New York, 1971, Chapter 3; (e) J.R. Golligly, C.J. Hawkins, and J.K. Beattie, *Inorg. Chem.*, **10**, 317 (1971), and references therein.

(17) L.J. Wilson and I. Bertini, *Chem. Commun.*, 1589 (1970).

(18) A.Y. Girgis and R.C. Fay, *J. Amer. Chem. Soc.*, **92**, 7061 (1970).

(19) (a) J.P. Fackler, Jr., T.S. Davis, and I.D. Chawla, *Inorg. Chem.*, **4**, 130 (1965); (b) T.S. Davis and J.P. Fackler, Jr., *ibid.*, **5**, 242 (1966).

(20) R.D. Gillard, *Inorg. Chim. Acta Reviews*, **1**, 69 (1967).

trum the ratio was separately determined for each possible independent pair of signals; the mean of values so obtained was averaged with values from all other spectra in the same solvent. The error limits shown in the table are standard deviations from the

mean of values from different spectra.

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